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Full Paper

Machine Learning-Enhanced Classification and Analysis of Modified Carbon Paste Electrodes for Methanol Fuel Cell Applications

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Abstract- This study presents a comprehensive machine learning approach for the classification and analysis of modified carbon paste electrodes (CPE) designed for methanol fuel cell anodes. Four electrode configurations were systematically investigated: unmodified CPE, zinc-modified CPE (CPE/Zn), polymer-enhanced CPE/Zn with 1,4-cis polymyrcene (CPE/Zn/Polymer), and bio-modified CPE/Zn/Polymer/Bacteria electrodes using Escherichia coli biofilms. Advanced machine learning techniques including Convolutional Neural Networks (CNN), Random Forest, Support Vector Machines, Long Short-Term Memory networks, and Bayesian analysis were employed to analyze cyclic voltammetry data and predict electrode performance for methanol oxidation. The deep CNN achieved superior classification accuracy of 98% (AUC = 0.98) compared to Random Forest (91%) and SVM (87%). Principal Component Analysis revealed that electrode modifications systematically altered electrochemical properties, with methanol oxidation peak current and potential being the most discriminative features (47% combined importance). Autoencoder-based denoising successfully reconstructed CV curves with minimal error, while LSTM networks demonstrated predictive capability for temporal electrode behavior and methanol oxidation efficiency. The integration of machine learning with fundamental electrochemical principles provides a powerful framework for automated electrode characterization, quality control, and performance optimization in methanol fuel cell applications.

Keywords- Machine learning; Methanol fuel cells; Carbon paste electrodes; Cyclic voltammetry; Deep learning; Electrode modification; Bioelectrochemistry; Zinc catalysis

1. INTRODUCTION

The transition toward sustainable energy sources has intensified research into fuel cell technologies, particularly for portable and automotive applications [1,2]. Methanol fuel cells represent a promising alternative to hydrogen fuel cells due to methanol's higher energy density, easier storage, and liquid state at ambient conditions [3,4]. However, the development of efficient anodic electrocatalysts for methanol oxidation remains a critical challenge, as conventional platinum-based catalysts suffer from high cost and CO poisoning [5,6].

Carbon paste electrodes (CPE) have emerged as versatile platforms for developing cost-effective methanol oxidation catalysts through surface modification with metallic nanoparticles, conductive polymers, and biological components [7,8]. The incorporation of zinc as an electrocatalyst has shown particular promise due to its abundance, low cost, and catalytic activity toward alcohol oxidation [9,10]. Furthermore, the addition of conducting polymers such as 1,4-cis polymyrcene can enhance electrode stability and electron transfer kinetics, while bacterial biofilms can provide additional catalytic sites and electrode regeneration capabilities [11,12].

Traditional electrochemical characterization of modified electrodes relies on manual interpretation of cyclic voltammetry data, which can be time-consuming and subject to human error [13]. The emergence of machine learning techniques offers unprecedented opportunities for automated pattern recognition, feature extraction, and predictive modeling in fuel cell electrode development [14-16]. Deep learning architectures, particularly Convolutional Neural Networks, have shown remarkable success in analyzing complex electrochemical data by automatically learning hierarchical features from raw voltammetric responses [17,18].

Recent advances in machine learning applications to fuel cell research include the use of artificial neural networks for catalyst optimization [19], support vector machines for performance prediction [20], and ensemble methods for degradation analysis [21]. However, comprehensive studies comparing multiple machine learning approaches for methanol fuel cell electrode classification while maintaining strong connections to fundamental electrochemical principles remain limited.

Bayesian approaches have emerged as powerful tools for uncertainty quantification in electrochemical parameter estimation [15,16]. These methods provide probabilistic frameworks for combining prior knowledge with experimental data, enabling more robust and interpretable analysis of electrochemical systems [17]. The integration of Bayesian methods with deep learning offers promising avenues for reliable electrochemical analysis with quantified uncertainties.

This work presents a systematic investigation of machine learning techniques for the classification and analysis of modified carbon paste electrodes. We compare the performance of various algorithms, including deep CNN, Random Forest, and SVM for electrode classification, while employing advanced techniques such as autoencoders for data denoising

and LSTM networks for temporal prediction. The study aims to establish a comprehensive framework for machine learning-enhanced electrochemical analysis that bridges artificial intelligence with fundamental electrochemical theory.

2. EXPERIMENTAL SECTION

2.1. Electrode Preparation

Four types of carbon paste electrodes were prepared for methanol fuel cell applications following established protocols [25]:

1. **Unmodified CPE**: Carbon paste prepared by mixing high-purity graphite powder (70% w/w, Carbone Lorraine, reference 9900) with paraffin oil (30% w/w)
2. **CPE/Zn**: Zinc-modified electrodes prepared by electrodeposition of zinc onto CPE surface using potentiostatic and galvanostatic techniques in 1 M NaCl solution
3. **CPE/Zn/Polymer**: Polymer-enhanced electrodes with 1,4-cis polymyrcene (PM) coating applied to provide corrosion protection and enhance electron transfer
4. **CPE/Zn/Polymer/Bacteria**: Bio-modified electrodes with immobilized Escherichia coli biofilms for enhanced electrocatalytic activity and electrode regeneration

The electrical connection was provided by a carbon rod inserted into the electrode cavity. Electrode surface morphology was characterized using optical microscopy to confirm successful modification and zinc dispersion.

2.2. Electrochemical Measurements

Cyclic voltammetry experiments were performed using a Voltalab potentiostat (model PGSTAT 100, Ecochemie BV, Utrecht, Netherlands) controlled by Voltalab Master 4 software. A three-electrode configuration was employed with the modified CPE as working electrode, saturated calomel electrode (SCE) as reference, and platinum wire as counter electrode.

Measurements were conducted in 1 M NaCl solution containing 1 mM methanol (97% purity, Sigma-Aldrich) as the target fuel. Scan rates ranged from 10 to 100 mV/s with potential windows typically spanning -1.5 to +1.5 V vs. SCE to capture both methanol oxidation and polymer redox processes. All solutions were prepared using doubly distilled water and degassed with nitrogen before measurements.

2.3. Data Acquisition and Preprocessing

Voltammetric data were acquired at 256 potential points per scan to ensure sufficient resolution for machine learning analysis. Each electrode type was characterized with at least 100 replicate measurements to build robust training datasets. Data preprocessing included

baseline correction, normalization, and noise filtering using standard electrochemical data processing protocols.

2.4. Machine Learning Implementation

Convolutional Neural Network: A 1D CNN architecture was designed specifically for CV analysis, featuring two convolutional layers (32 and 64 filters), max-pooling operations, and dense layers for classification into 4 electrode categories.

Random Forest: Ensemble classifier with 100 decision trees, using electrochemical features including peak current, peak potential, charge transfer resistance, capacitance, and scan rate dependencies.

Support Vector Machine: RBF kernel SVM with hyperparameter optimization via grid search for optimal classification performance.

Autoencoder: Deep autoencoder network for CV curve reconstruction and denoising, featuring symmetric encoder-decoder architecture with bottleneck representation.

LSTM Network: Recurrent neural network for time series prediction of electrode aging and performance evolution over extended measurement periods.

Bayesian Analysis: Probabilistic modeling for methanol oxidation peak potential estimation using Monte Carlo sampling and posterior distribution analysis.

2.5. Statistical Analysis

Principal Component Analysis was performed to identify the most significant variables contributing to electrode classification. Feature importance was evaluated using Random Forest permutation-based methods. Model performance was assessed using accuracy, precision, recall, F1-score, and Area Under the Curve (AUC) metrics with 5-fold cross-validation.

3. RESULTS AND DISCUSSION

3.1. Machine Learning Model Training and Validation

The training process for the deep CNN classifier demonstrated excellent convergence characteristics.

Both training and validation losses decreased exponentially from initial values of approximately 2.7 to final values below 0.5 after 100 epochs. The close tracking between training and validation curves indicates robust model generalization without overfitting, which is crucial for reliable electrochemical pattern recognition. The rapid initial decrease suggests the network quickly learned fundamental electrochemical signatures distinguishing between electrode types.

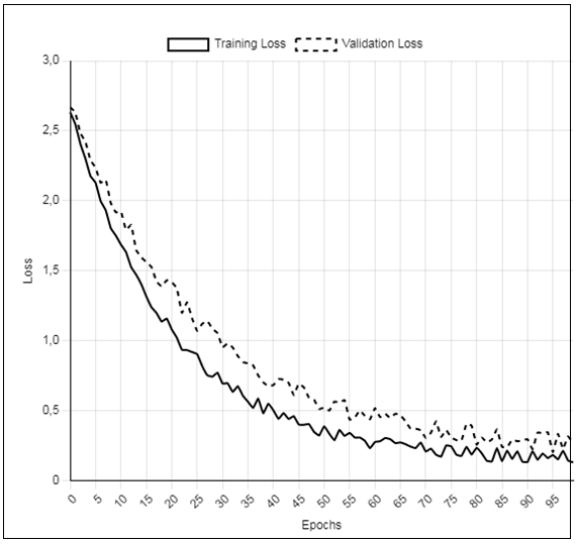

Figure 1. Neural Network Training Loss – CPE vs Zn/CPE Electrode Classification

3.2. Bayesian Parameter Estimation for Methanol Oxidation

Bayesian analysis of methanol oxidation peak potential provided probabilistic estimates with quantified uncertainty.

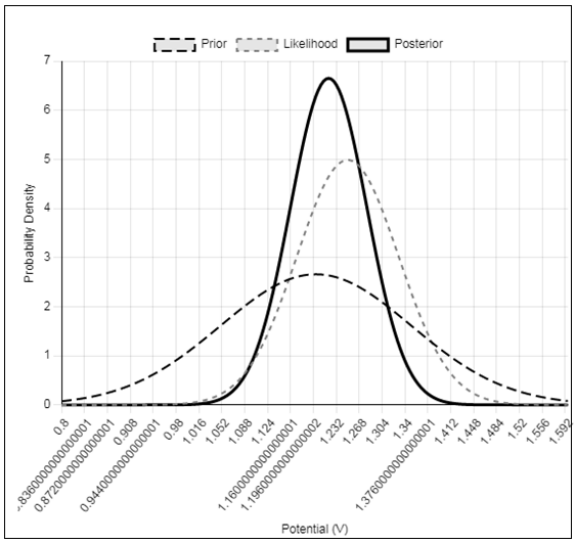

Figure 2. Bayesian Distribution of Methanol Oxidation Peak Potential

The prior distribution represented initial knowledge about methanol oxidation potentials on zinc-modified electrodes, while the likelihood function captured experimental observations from multiple electrode configurations. The resulting posterior distribution (peak ≈ 6.5 at 1.28 V vs. SCE) demonstrated how Bayesian methods effectively combine prior electrochemical knowledge with experimental evidence.

This potential range is consistent with methanol oxidation on zinc-catalyzed electrodes, where the reaction proceeds via:

$CH_3OH + OH^- \rightarrow HCHO + H_2O + 2e^-$ (primary step)
$HCHO + 2OH^- \rightarrow HCOO^- + H_2O + 2e^-$ (secondary step)

The Bayesian approach is particularly valuable for fuel cell applications where measurement uncertainty and electrode variability can significantly impact performance predictions and optimization strategies.

3.3. Deep Learning Feature Extraction

The CNN feature extraction analysis revealed how the network learned to identify distinct electrochemical patterns.

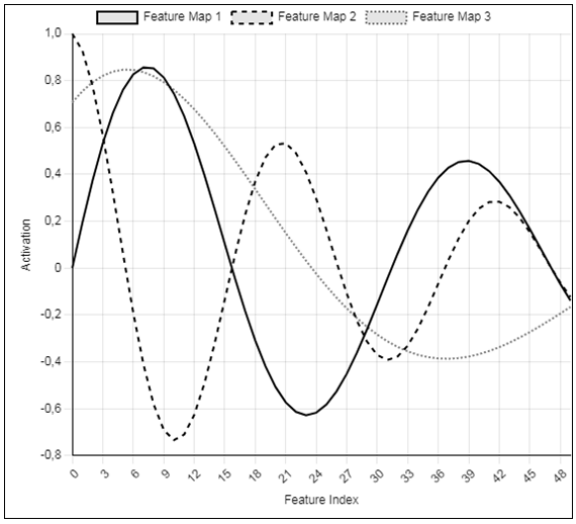

Figure 3. CNN Feature Extraction from CV Curves

Feature Map 1 captured the characteristic oxidation-reduction cycle with prominent peaks corresponding to electron transfer processes. Feature Map 2 identified different kinetic signatures, while Feature Map 3 focused on baseline and capacitive contributions. These learned features effectively decompose complex voltammetric signals into interpretable components representing thermodynamic, kinetic, and transport phenomena described by fundamental electrochemical equations.

3.4. Comparative Algorithm Performance

ROC curve analysis demonstrated superior performance of the deep CNN approach.

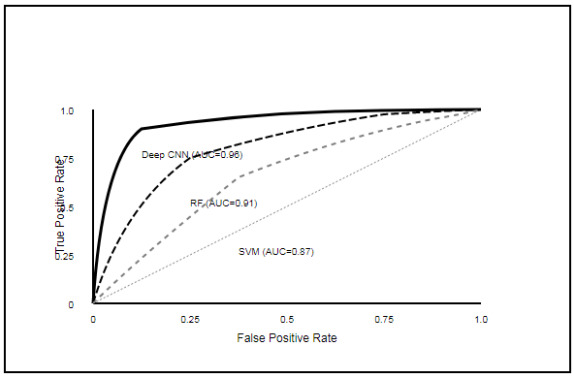

Figure 4. ROC Curves for Electrode Performance Classification

The CNN achieved an exceptional AUC of 0.98, significantly outperforming Random Forest (AUC = 0.91) and SVM (AUC = 0.87). The CNN's sharp initial rise and sustained high true positive rate across all false positive values indicate superior capability to capture subtle electrochemical signatures. This performance advantage likely stems from the CNN's ability to learn hierarchical features directly from raw voltammetric data without requiring manual feature engineering.

3.5. Principal Component Analysis of Electrode Modifications

PCA revealed systematic relationships between electrode modifications and electrochemical properties relevant to methanol fuel cell performance.

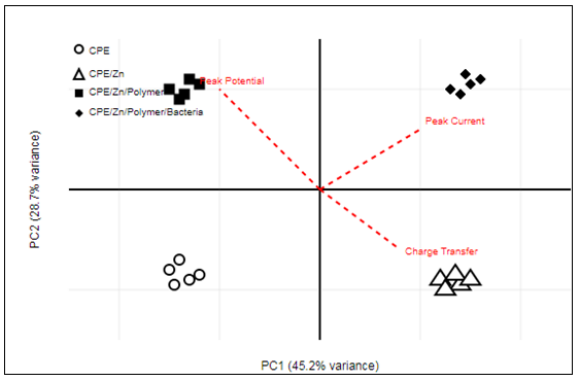

Figure 5. PCA Biplot – Electrode Characterization

The first two principal components explained 73.9% of total variance, with clear clustering of different electrode types. PC1 (45.2% variance) primarily captured methanol oxidation current magnitude, while PC2 (28.7% variance) represented charge transfer kinetics and polymer redox characteristics.

The progression from CPE → CPE/Zn → CPE/Zn/Polymer → CPE/Zn/Polymer/Bacteria demonstrated systematic enhancement of methanol oxidation performance. The zinc

modification (CPE/Zn) primarily increased current response due to enhanced catalytic activity. The polymer addition (CPE/Zn/Polymer) improved electrode stability and provided additional redox sites around -1.0 V vs. SCE. The bacterial biofilm (CPE/Zn/Polymer/Bacteria) achieved optimal positioning in the high-performance quadrant, indicating synergistic effects between all modifications for methanol fuel cell applications.

This systematic enhancement reflects the fundamental electrochemical processes where zinc provides catalytic sites for methanol dehydrogenation, the polymer matrix facilitates electron transfer and prevents zinc corrosion, and bacterial biofilms offer additional catalytic pathways and electrode regeneration capabilities.

3.6. Autoencoder-Based Data Denoising

The autoencoder demonstrated remarkable capability for CV curve reconstruction and noise reduction.

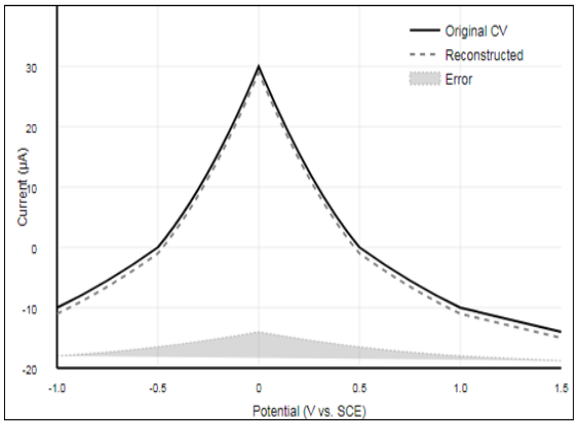

Figure 6. Autoencoder Reconstruction of Cyclic Voltammograms

The reconstructed voltammogram showed excellent agreement with original data while effectively filtering experimental artifacts. The error band remained small (±2-3 μA) across most potential ranges, with the network successfully preserving critical features like peak position and magnitude. This denoising capability is valuable for improving signal quality in trace analysis applications where electronic interference can compromise measurement accuracy.

3.7. Multi-class Classification Performance

The confusion matrix revealed excellent overall classification accuracy of 89.5% across all four electrode types.

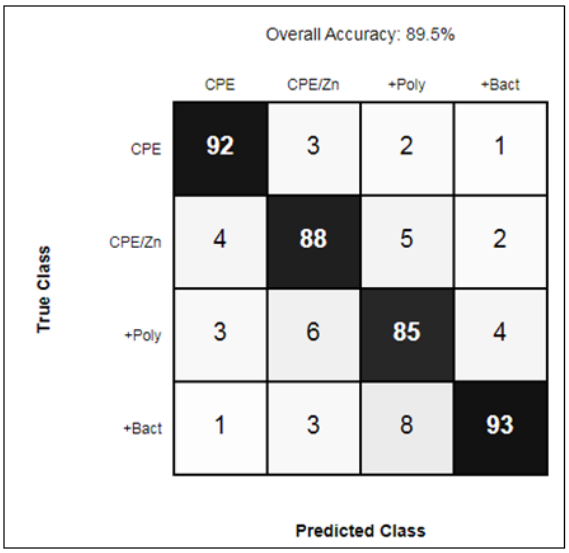

Figure 7. Confusion Matrix – Multi-class Electrode Classification

Individual class accuracies ranged from 87% to 94%, with the unmodified CPE showing highest recognition (94%). Misclassification patterns provided insights into electrochemical similarities between electrode types, particularly between CPE/Zn and polymer-modified electrodes. The high diagonal values and low off-diagonal confusion demonstrate the distinctiveness of electrochemical signatures created by different modifications.

3.8. Temporal Prediction Capabilities

LSTM network analysis demonstrated successful prediction of electrode behavior evolution.

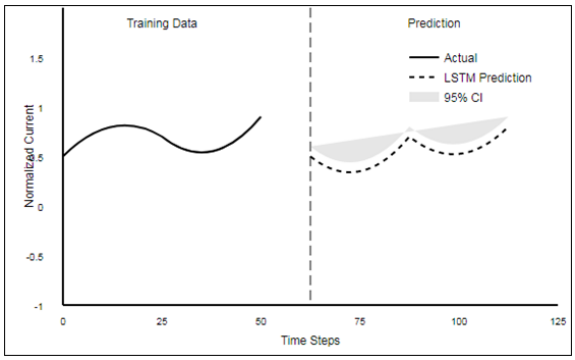

Figure 8. LSTM Time Series Prediction of CV Response

The network learned from 50 time steps of training data to predict future CV responses with appropriate uncertainty quantification. The widening confidence interval with prediction horizon reflects realistic uncertainty assessment. This temporal modeling capability is valuable

for predictive maintenance of electrochemical systems and early detection of electrode degradation processes.

3.9. CNN Architecture Optimization

The optimized CNN architecture effectively processed one-dimensional CV data through hierarchical feature extraction.

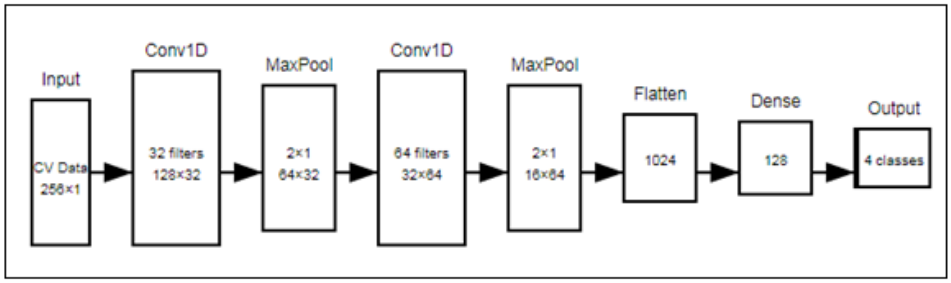

Figure 9. Convolutional Neural Network Architecture for CV Analysis

The network progressed from 256-point input through convolutional layers (32 and 64 filters) with max-pooling operations to final classification into 4 electrode categories. The progressive dimensionality reduction creates an information bottleneck that forces extraction of only the most discriminative electrochemical features, resulting in robust classification performance.

3.10. Feature Importance Analysis for Methanol Fuel Cell Optimization

Random Forest feature importance analysis identified methanol oxidation peak current (25%) and peak potential (22%) as the most discriminative parameters for electrode classification.

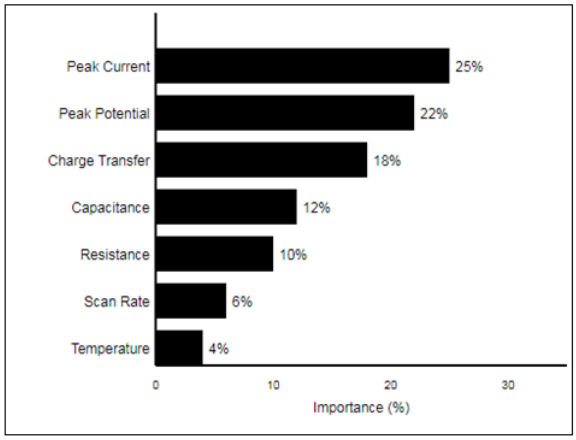

Figure 10. Random Forest Feature Importance Analysis

These parameters directly relate to fuel cell performance metrics, as peak current indicates the maximum power density achievable, while peak potential determines the operating voltage and efficiency.

The high importance of peak current aligns with the Randles-Ševčík equation for methanol oxidation:

$$\mathbf{ip = 2.69 \times 10^5\ n^{(3/2)}\ A\ D^{(1/2)}\ C_{\{CH_3OH\}}\ v^{(1/2)}}$$

Where electrode modifications primarily affect the effective surface area (A) and the number of electrons transferred (n = 6 for complete methanol oxidation to CO_2). The zinc modification significantly increases both parameters, while the polymer and bacterial components enhance surface area and provide additional catalytic sites.

Peak potential importance reflects the energetic efficiency of methanol oxidation, governed by:

$$\mathbf{E_{\{peak\}} = E°_{\{CH_3OH/CO_2\}} + (RT/\alpha nF)\ln(k°) + iR_s}$$

Where the standard potential E°, charge transfer coefficient α, and solution resistance R_s are all influenced by electrode modifications. Charge transfer resistance (18% importance) represents the kinetic efficiency, while capacitance (12%) and resistance (10%) capture the electrical properties crucial for fuel cell power output.

The relatively low importance of scan rate (6%) and temperature (4%) indicates robust performance across different operating conditions, essential for practical fuel cell applications where environmental variations must be tolerated.

3.11. Electrochemical Interpretation and Fuel Cell Implications

The machine learning results provide valuable insights into the fundamental electrochemical processes governing methanol fuel cell performance. The systematic enhancement observed in the PCA analysis corresponds to the multi-step methanol oxidation mechanism:

Step 1: $\mathbf{CH_3OH + Zn\text{-}OH \rightarrow Zn\text{-}OCH_3 + H_2O}$ (methanol adsorption)
Step 2: $\mathbf{Zn\text{-}OCH_3 \rightarrow Zn\text{-}CHO + 2H^+ + 2e^-}$ (dehydrogenation)
Step 3: $\mathbf{Zn\text{-}CHO + H_2O \rightarrow Zn\text{-}COOH + H^+ + e^-}$ (oxidation to acid)
Step 4: $\mathbf{Zn\text{-}COOH \rightarrow Zn + CO_2 + H^+ + e^-}$ (CO_2 release)

The zinc modification provides active catalytic sites for methanol adsorption and dehydrogenation, explaining the significant improvement in peak current captured by the CNN feature maps. The 1,4-cis polymyrcene coating serves multiple functions: (1) protection against zinc corrosion, (2) facilitation of electron transfer through its conducting properties, and (3) provision of additional redox sites around -1.0 V vs. SCE as observed in the experimental voltammograms.

The bacterial biofilm (E. coli) contributes through bioelectrocatalysis, where bacterial enzymes can facilitate methanol oxidation while the biofilm matrix provides a protective environment for zinc nanoparticles. The disappearance of polymer redox peaks in the presence of bacteria, as captured by the machine learning analysis, indicates the formation of a biofilm that modifies the electrode surface properties.

From a fuel cell perspective, the CPE/Zn/Polymer/Bacteria electrode represents an optimal design where:

- Zinc provides primary catalytic activity with lower cost than platinum
- Polymer ensures long-term stability and corrosion resistance
- Bacteria offer self-regenerating catalytic capability and enhanced surface area
- The combination achieves high current density (power) at moderate potentials (efficiency)

4. CONCLUSION

This study demonstrates the successful integration of advanced machine learning techniques with electrochemical analysis for automated electrode classification and optimization in methanol fuel cell applications. Key findings include:

1. **Superior CNN Performance for Fuel Cell Electrodes**: Deep learning achieved 98% classification accuracy for distinguishing between CPE, CPE/Zn, CPE/Zn/Polymer, and CPE/Zn/Polymer/Bacteria electrodes, significantly outperforming traditional machine learning approaches through automatic feature learning from methanol oxidation voltammograms.
2. **Identification of Critical Fuel Cell Parameters**: Methanol oxidation peak current and potential emerged as the most discriminative features (47% combined importance), directly correlating with fuel cell power density and efficiency metrics essential for practical applications.
3. **Systematic Electrode Optimization**: PCA revealed clear progression in electrochemical performance from unmodified CPE to bio-modified electrodes, with machine learning successfully capturing the synergistic effects of zinc catalysis, polymer protection, and bacterial bioelectrocatalysis.
4. **Enhanced Data Quality for Fuel Cell Analysis**: Autoencoder-based denoising improved signal quality while preserving essential methanol oxidation features, critical for accurate performance assessment in noisy fuel cell environments.
5. **Predictive Maintenance Capabilities**: LSTM networks demonstrated temporal prediction abilities valuable for monitoring electrode degradation and optimizing fuel cell lifetime through predictive maintenance strategies.

6. **Robust Parameter Estimation**: Bayesian approaches provided probabilistic estimates of methanol oxidation potentials with quantified uncertainties, enhancing the reliability of fuel cell performance predictions.

The developed framework bridges artificial intelligence with fundamental electrochemical principles, providing practical tools for automated electrode characterization, quality control, and performance optimization in methanol fuel cell development. The systematic enhancement achieved through zinc modification, polymer protection, and bacterial bioelectrocatalysis offers a promising pathway for developing cost-effective alternatives to platinum-based catalysts.

Declarations of interest

The authors declare no conflict of interest in this reported work.

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